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Patent Abstracts of Japan

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APPLICANT : NITTO BOSEKI CO LTD;

INVENTOR : SUGANO KOJI;

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TITLE : BUNDLING AGENT FOR GLASS FIBER AND FABRIC OF GLASS FIBER

ABSTRACT : PROBLEM TO BE SOLVED: To obtain a fabric almost free from fluffing in a working process and having satisfactory suitability to impregnation with a resin by blending a bundling agent for glass fibers with specified inorg. solid particles and sticking a specified amt. of the solid particles to glass fibers.

SOLUTION: A bundling agent for glass fibers deoiled by heating is blended with inorg. solid particles of at least one selected from among colloidal silica, light calcium carbonate, kaolin and fine particle-shaped talc having 5-2,000nm average particle diameter and the solid particles are stuck to glass fibers by 0.001-2.0wt.% (expressed in terms of solid).

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(54) 【発明の名称】 ガラス繊維用集束剤及びガラス繊維織物

(57) 【要約】

【課題】 樹脂含浸性の良いガラス繊維織物を提供する。

【解決手段】 ガラス繊維を紡糸するとき付着させる集束剤中に5-2000nmのコロイダルシリカ、軽質炭酸カルシウムなどの無機固体粒子を配合した。集束剤を付着させることによりヤーンを構成するガラス繊維の周囲に粒子が付着し隙間を作るので、このヤーンで製織した織物は樹脂の含浸性が良い。

$$k = -\frac{4}{3} \text{ or } 3 \Rightarrow k = -\frac{4}{3}, 3$$

眼処理を公知の微粉并十重を小くし、招度底へし

立ちが増える、この現象は円筒の上に巻き取るガラス繊維が増えると直径が大きくなり、巻き取るとき次第にガラス繊維に掛る張力が増え内部のガラス繊維層を押し潰すような力が発生し一部のガラス繊維が切断されるものと思われる。あるいはガラス繊維を製織したガラス繊維織物に樹脂を含浸する時間を短縮し積層板の製造能率を上げ積層板の製造コストを低減したいという課題について解決が望まれている。

【0008】本発明は、上記のような諸問題を解決するために新たに開発されたガラス繊維用集束剤に関するもので、ガラス繊維紡糸時に優れたケーギ形状安定性を有し、且つ、加工工程においても毛羽発生が巻取量を増加しても、従来の巻量的場合と同様に極めて少なく、製織されたガラス繊維織物の樹脂含浸性の良好なガラス繊維ヤーンを得ることのできる集束剤及びこの集束剤を付着させたガラス繊維を提供することを目的としている。

【0009】

【課題を解決するための手段】本発明は、ガラス繊維用集束剤中にコロイダルシリカ、カオリン、軽質炭酸カルシウム、などの無機質固体粒子を少なくとも1種以上配合し、それらの固体粒子をガラス繊維に固形分で0.001-2.0重量%付着させることにより上記の課題を解決した。

【0010】

【発明の実施の態様】このような集束剤にコロイダルシリカなどの無機固体粒子を添加して前述の課題を解決しようとするものであるが、界面活性剤などにはコロイダルシリカと適合しないものがあり、これらを配合したときゲル化、分離などの起きる場合があり配合される集束剤の成分は、それを考慮して決められる。集束剤の成分が澱粉を主体とした従来のタイプのものに有効であるが、PVA（ポリビニルアルコール）、ウレタン樹脂、エポキシ樹脂など合成樹脂系の材料が使用される場合も有効である。本発明に使用される無機固体粒子にはカオリン、軽質炭酸カルシウム、微粒タルク、粉末状ヒュームドシリカ（日本アエロジル社製）、コロイダルシリカなどがある。これらの粒子は加熱脱油の温度で分解しないもので、粒子の大きさは5-2,000nmのものが使用できる。

【0011】コロイダルシリカは粒子の大きさが5-100nm程度である無定形シリカが水や有機溶媒に沈降

せず安定に分散しているものであり、別名シリカゾルとも呼ばれている。このコロイダルシリカは、ケイ酸ソーダ水溶液（水ガラス）やケイ酸エステル、ハロゲン化ケイ素の加水分解等によって得られるケイ酸を、高重合化し、コロイドの大きさに成長させることによって得られる。このようにして得られるコロイダルシリカの粒子は、一般に球状であり、内部の大部分はシロキサン結合（ $-Si-O-Si-$ ）であるが、粒子表面層はシラノール基（ $-SiOH$ ）で覆われている。

【0012】本発明はコロイダルシリカなどの無機質固体粒子一種を集束剤と混合して使用してもよく、二種以上の無機質固体粒子を集束剤と混合して使用してもよい。本発明の無機質固体粒子と混合して使用する集束剤用化合物には、相溶性に問題がないものであれば使用できる。

【0013】集束剤中のコロイダルシリカなどの無機固体粒子の固形分含有量は、0.001-20.0重量%で、好ましくは0.01-5.0重量%で、さらに好ましい量は0.1-2.0重量%である。0.001重量%以下ではコロイダルシリカなどの無機固体粒子の樹脂含浸促進効果が出るだけの量をガラス繊維に付着させることが出来ず、20.0重量%以上ではガラス繊維に塗布することが出来ない。

【0014】本発明の無機固体粒子を含有する集束剤を付着させたガラス繊維ストランドからヤーンを製造するが、ガラス組成、フィラメントの直径、フィラメントの断面形、繊維束を構成するフィラメント数により限定されず、任意の繊維束に適用可能である。ヤーンに付着した本発明の無機固体粒子を含有する集束剤の固形分量は、0.001-10.00重量%で、好ましくは0.1-4.00重量%で、さらに好ましくは0.3-1.50重量%である。0.001重量%では集束剤としての効果がなく、10.0重量%以上では繊維束が硬くなり過ぎガラスクロスを織る上で問題となる。

【0015】ガラス繊維に付着している無機固体粒子は固形分量で0.001-2.0重量%、好ましくは0.01-0.98重量%、更に好ましくは0.1-0.6重量%である。

【0016】

【実施例】

<実施例1>

ハイアミロース型トウモロコシエーテル化澱粉	4.0重量%
水素添加綿実油	0.5重量%
パラフィンワックス	1.0重量%
ポリオキシエチレンポリオキシプロピレンエーテル	0.2重量%
テトラエチレンペンタミンとステアリン酸の反応生成物	0.3重量%
ホルマリン（40重量%水溶液）	0.1重量%
コロイダルシリカ（20重量%水溶液）	0.5重量%

【0017】実施例1の集束剤100kgの調合方法は、ル化澱粉4kgを水80kg中に分散させ、95℃まで

(A液)。別容器に、加熱溶解された水素添加綿実油500g、パラフィンワックス1000g、及びポリオキシエチレンポリオキシプロピレニール200gを秤量し、ホモキサーで撹拌しながら熱湯を加え、反転乳剤化後、熱湯で希釈して5kgとする(B液)。また、別容器に、ナトラエチレンベンタミニンとステアリン酸の縮合物の酢酸活性化物を300g秤量し、熱湯で希釈し3kgとする(C液)。また、ホルマリンを100g秤量し、水で希釈して1kgとする(D液)。さらに、コロイダルシリカ「スノーテック」(日産化学工業(株)製、粒子径10-20nm、SiO2 20重量%) 500gを秤量し、水で希釈して5kgとする(E液)。A液にB液、C液、D液、及びE液を順次加えた後、水を加えて総重量を100kgに合わせ、60℃で保温する。

【0018】本集束剤をガラス繊維にローラーアプリーク

ハイアミロース型トウモロコシエーテル化澱粉

通常型トウモロコシ架橋化澱粉

水素添加綿実油

パラフィンワックス

ポリオキシエチレンポリオキシプロピレニール

ナトラエチレンベンタミニンとステアリン酸の反応生成物

ホルマリン

コロイダルシリカ(商品名: Cataloid S-30H、触媒化成工業(株)製、粒子径10-20nm、SiO2含有量30重量%)

固形分換算

0.5重量%

3.5重量%

1.5重量%

1.0重量%

1.0重量%

1.0重量%

0.2重量%

0.4重量%

0.1重量%

本集束剤をG75のガラス繊維に固形分で0.97重量%付着させた他は実施例1と同様に実施した。表1に、クーキ形状安定性、ガラス繊維織物の品質を示すが、極めて安定したクーキ形状、そして、優れた樹脂含浸性を示した。

【0020】<実施例3>実施例1においてコロイダルシリカに代えて平均粒径40nmの軽質炭酸カルシウムを0.4重量%使用したことを除いては実施例1と同様に実施した。試験結果は表1に示す。

【0021】<比較例1>コロイダルシリカ0.5重量%の代わりに水を加えることを除いては、実施例1と同様に実施し、得られた結果を表1に示す。

【0023】

【評価方法】

1.クーキの形状安定性

使用樹脂組成

エピコート1001(シエル化学社製エポキシ樹脂) 100重量部

ジシアノジエミド

ヘンシルジメチルアミン

メチルオキシトール

【0025】

【効果】本発明によれば、巻き取ったクーキの外形の変形を少なくすることができるので、得られたガラス繊維の切断が少なくなり、ヤーン及びガラス繊維織物の毛羽

が少なく、またガラス繊維ヤーンを構成するガラス繊維の束全体に均一に固体粒子が付着している

で、織物にした場合糸糸と糸糸が最も密度高くクロスする部分の糸にも固体粒子による繊維間の隙間が確保され

る部分の糸にも固体粒子による繊維間の隙間が確保され

る部分の糸にも固体粒子による繊維間の隙間が確保され

均一な樹脂含浸と含浸時間の短縮が可能となった。

【0026】

表1

	形状安定性 (変形)	毛羽 (等級)	樹脂含浸性 (等級)
実施例1	なし	1	1
実施例2	なし	2	1
実施例3	なし	2	2
比較例1	あり	4	5

[English Translation]

(19) Japanese Patent Office

(12) Laid-Open Patent Gazette (A)

(11) Laid-Open Patent Application No. Hei-9 (1997)-208268 A

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Number of Claims 3, FD (Patent Gazette of 5 pages in the total)

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(22) Filing Date: February 2, Year of Heisei-08 (1996)

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Fukushima Prefecture)

(54) [Title of Invention] GLASS FIBER SIZING AGENT AND GLASS
FIBER FABRIC

(57) [Abstract]

[Problem to be Solved] To provide glass fiber fabric well adapted for resin
impregnation.

[Means for Solution] Colloidal silica, light precipitated calcium carbonate or
other inorganic solid particles of 5~2000nm are included in a glass fiber
sizing agent applied during the spinning of glass fiber. The deposition of the
sizing agent causes the particles to adhere and form spaces around the
glass fiber which constitutes yarns so that a resin can be well impregnated
in glass fiber fabric made from the yarns.

10-38

[Claims]

[Claim 1] A glass fiber sizing agent to be de-oiled by heating, wherein the sizing agent contains inorganic solid particles.

[Claim 2] A glass fiber sizing agent according to Claim 1, wherein the sizing agent contains at least a kind of inorganic solid particles having an average particles size of 5~2000nm, and selected from the group consisting of colloidal silica, light precipitated calcium carbonate, kaolin, finely divided talc.

[Claim 3] Glass fiber fabric comprising glass fiber yarn wherein inorganic solid particles according to Claim 2 are deposited in an amount of 0.001~2.0% by weight, as solids.

[Detailed Explanation of Invention]

[0001]

[Field of Invention] The present invention relates to a sizing agent for glass fiber and glass fiber processed with the sizing agent.

[0002]

[Prior Art] A sizing agent for glass fiber is applied, during the high speed spinning of glass fiber from molten glass, by coating multiple glass filaments on a roller applicator or a belt applicator immediately after the spinning to protect the glass fiber. The glass fiber sizing agent can be largely divided into the agent for yarns and the agent for roving. In the following, the explanation shall be made about the agent for yarns. Glass fiber bundles processed with the sizing agent are wound on a pipe as a cake. The cake is appropriately dried, twisted on a twister and rewound on a bobbin to become glass fiber yarns. The yarns are mainly woven to form fabric, and after the sizing agent is removed by a de-oiling treatment, such as hot de-oiling by high temperature heating for oxidation removal, water

de-oiling by water washing or washing using a vibration washer, etc., a surface treatment agent, such as silane coupling agent etc., is generally applied on the surface of the glass fiber to improve resin adhesion and heat resistance.

[0003] After the fabric is impregnated with an uncured resin or a resin having a reduced viscosity with a solvent content and solvents are removed, a number of thus processed fabrics are plied and pressed to form a laminate. Prior art sizing agents used for this purpose have been mainly based on starch which can prevent fiber from fluffing and can be easily removed by the de-oiling.

[0004] However, some of recent sizing agents for yarns may contain a synthetic resin material such as polyvinyl alcohol (PVA), urethane resin, epoxy resin, etc. Starch used for the starch-based sizing agent is available as variously processed materials, including the following: natural, unprocessed starch such as corn starch, potato starch, etc.; chemical modifications thereof, for example, products by etherification such as hydroxyalkylation, products by esterification such as acetylation, cross-linked products by reaction with a cross-linking agent such as epichlorohydrin, etc.; lower viscosity products prepared by reducing the known molecular weight of starch by acid treatment etc. to obtain the lower viscosity; etc. An example of a prior art sizing agent formulation may be specifically described as follows: 2~10% by weight of a starch-based material; 0.2~5% by weight of a lubricant; 0.05~1.0% by weight of a surface active agent; 0.01~0.5% by weight of an antiseptic agent; and the rest of water.

[0005] Starch is used to form a film for the protection of fiber from all the mechanical bending and frictions by bonding and bundling several

hundreds of glass fiber filaments to form a strand. Starch materials often used include corns, potatoes, etc., and chemical modifications thereof, for example, products by etherification such as hydroxyalkylation, etc., are also frequently used. A lubricant is used for the reduction of mechanical frictions to protect the fiber by providing the strand with lubrication. Frequently used kinds of the lubricant include hardened oils prepared by the hydrogenation of animal or vegetable oil, paraffin wax, esters of a higher saturated fatty acid and a higher saturated alcohol, etc. Cationic lubricants are used for the purpose of reducing the mutual friction of filaments in the strand by softening glass fiber, and examples thereof include alkyl quaternary ammonium salts, amides obtained by the condensation of polyethylene amide with a higher fatty acid, imidazoline, etc. Surface active agents are mainly used as an emulsifier for the lubricant, and frequently used examples of the surface active agent include polyoxyethylene alkyl ether, etc. An antiseptic agent mainly used is formalin.

[0006] As a glass fiber sizing agent containing colloidal silica as solid particles, Japanese Published Patent Application Hei-01 (1989)-203247 B discloses a glass fiber roving binder for FRP spray-up, wherein colloidal silica is formulated in polyvinyl acetate. Also, Japanese Laid-Open Patent Application Hei-06 (1994)-248572 A discloses a technology wherein glass fiber fabric impregnated with colloidal silica and dried is opened by means of a vibration washer, and subsequently, fiber fabrics impregnated with a resin are laminated and pressed under heating. The former teaching relates to reducing the sliding of glass fiber roving for improved cutting properties by the application of a sizing agent containing colloidal silica. The latter teaching relates to introducing colloidal silica among glass fibers

to provide spaces among fibers for improved resin impregnation by applying colloidal silica to glass fiber fabric and subsequent opening by means of a vibration washer, etc. However, because of the warp and weft crossings in the fabric, it has been considerably difficult to homogeneously introduce colloidal silica when the fabric is observed from the micro view point.

[0007]

[Problem to be Solved by Invention] Sizing agents constituted by combination of these compounds have excellent properties and have been practically used. However, as the speed and efficiency of glass fiber production become increased, the increased amount of glass fiber is wound up at one time and the cake becomes larger. As the cake package becomes larger, a part of fiber is broken within the cake and more fluffing is caused to the glass fiber yarns. This phenomenon is assumedly caused as follows: as an increasing amount of glass fiber is wound up on a pipe to a larger diameter, an increasingly larger tension is applied to the glass fiber upon winding and a large force so as to crush the inner layer of glass fiber is generated, thus breaking a part of glass fiber. Otherwise, it has been desired to improve the efficiency of laminate production by reducing a time required for the resin impregnation of glass fiber fabric woven from glass fiber and thus to reduce the cost of laminate production.

[0008] The present invention relates to a newly developed glass fiber sizing agent to solve said problems, and the purpose of the present invention is to provide a sizing agent capable of producing glass fiber yarns with excellent cake shape stability during glass fiber spinning, with a similarly low level of fluffing during the step of fabrication as in the prior art winding amount even when the winding amount is increased, and with excellent resin

impregnation of glass fiber fabric woven from the glass fiber yarns, and glass fiber processed with the same sizing agent.

[0009]

[Means for Solution] The present invention has solved said problem by the use of a sizing agent containing at least a kind of inorganic solid particles such as colloidal silica, kaolin, light precipitated calcium carbonate, etc., and by the deposition of these solid particles on the glass fiber in an amount of 0.001~2.0% by weight, as solids.

[0010]

[Mode of Working Invention] Said problem is to be solved by the addition of inorganic solid particles such as colloidal silica, etc. to a sizing agent in this manner, but some surface active agents are incompatible with colloidal silica and inclusion thereof may sometimes cause gelation, separation, etc., and therefore, components for the sizing agent should be determined in consideration of these factors. The sizing agent component is effective for prior art type sizing agents mainly based on starch but also effective for sizing agents using synthetic resin materials such as polyvinyl alcohol (PVA), urethane resins, epoxy resins, etc. Inorganic solid particles to be used according to the present invention include kaolin, light precipitated calcium carbonate, finely divided talk, powdery fumed silica (made by Japan Aerosil Co., Ltd.), colloidal silica, etc. These particles to be used are not decomposed at a temperature for hot de-oiling and have a particle size of 5~2,000 nm.

[0011] Colloidal silica is amorphous silica in a stable dispersion without precipitation in water or organic solvents and having a particle size of approximately 5~100 nm, and is sometimes called silica gel. Colloidal silica can be obtained by the polymerization of silicic acid obtained by the

hydrolysis of aqueous sodium silicate solution (water glass), silicate esters or silicon halides, until the polymer size grows to a colloidal one. The particles of colloidal silica thus obtained are generally globular, and the most of the inner portions are constituted siloxane bonds ($-\text{Si}-\text{O}-\text{Si}-$) but the particles is covered with silanol groups ($-\text{SiOH}$) on the surface layer.

[0012] According to the present invention, a kind of inorganic solid particles such as colloidal silica can be used alone for blending in the sizing agent, or 2 or more kinds of inorganic solid particles can be used in combination for blending in the sizing agent. Any compound may be used in the sizing agent in blending with the inorganic solid particles according to the present invention, as far as it does not cause a problem in their compatibility.

[0013] A solid content of the inorganic solid particles such as colloidal silica, etc. in the sizing agent is 0.001~20.0% by weight, preferably 0.01~5.0% by weight, and more preferably 0.1~2.0% by weight. When the content is less than 0.001% by weight, the inorganic solid particles such as colloidal silica, etc. cannot be deposited on glass fiber in a sufficient amount for achieving their effect of promoting the resin impregnation, while the coating of the inorganic solid particles cannot be applied on glass fiber in excess of 20.0% by weight.

[0014] Glass fiber yarn is produced from the strands of glass fiber on which a sizing agent containing inorganic solid particles according to the present invention is deposited, but no restriction is placed on the glass composition, filament diameter, filament cross-section, and number of filaments constituting a fiber bundle, and the invention can be applied to any fiber bundles. A solid content of a sizing agent deposited on the yarn and containing inorganic solid particles according to the present invention is

0.001~10.00% by weight, preferably 0.1~4.00% by weight, and more preferably 0.3~1.50% by weight. If the content is less than 0.001% by weight, the effect as a sizing agent cannot be achieved, while the content in excess of 10.0% by weight produces too rigidly bundled glass fiber and causes difficulty in weaving glass fabric.

[0015] A solid content of inorganic solid particles to be deposited on glass fiber is 0.001~2.0% by weight, preferably 0.01~0.98% by weight, and more preferably 0.1~0.6% by weight.

[0016]

[Examples]

〈Example 1〉

Etherified amylose-rich corn starch	4.0% by weight
Hydrogenated cotton seed oil	0.5% by weight
Paraffin wax	1.0% by weight
Polyoxyethylene polyoxypropylene ether	0.2% by weight
Reaction product of tetraethylene pentamine with stearic acid	0.3% by weight
Formalin (an aqueous 4% by weight solution)	0.1% by weight
Colloidal silica (an aqueous 20% by weight solution)	0.5% by weight

[0017] A sizing agent in Example 1 was prepared in the amount of 100kg according to the following procedure: 4kg of etherified amylose-rich corn starch was dispersed in 80kg of water, the dispersion was heated to 95°C and stirred for 30 minutes at the temperature, and subsequently cooled to 65°C (as Solution A). In a separate vessel, 500g of hydrogenated corn seed oil, 1,000g of paraffin wax, and 200g of polyoxyethylene polyoxypropylene ether were taken in molten conditions, hot water was added under stirring

with a homogenizing mixer to a mixture thus obtained, after inversion emulsification. the emulsion was diluted with hot water to the amount of 5kg (as Solution B). In a further different vessel, 300g of the acetic acid-activated condensation product of tetraethylene pentamine with stearic acid was taken and diluted with hot water to the amount of 3kg (as Solution C). Also, 100g of formalin was taken and diluted with hot water to the amount of 1kg (as Solution D). In addition, 500g of colloidal silica (Snowtex ST-20 made by Nissan Chemical Industry Co., Ltd. and having the particle sizes of 10~20nm and the SiO₂ content of 20% by weight) was taken and diluted with water to the amount of 5kg (as Solution E).

Solutions B, C, D and E were successively added to Solution A, and the mixture was kept at 60°C after the total weight was adjusted to 100kg with the addition of water.

[0018] This sizing agent was applied to glass fiber on a roller applicator to the solid content of 0.90% by weight to form glass fiber strands, which were wound as cakes. The strands were further twisted to form yarns having G75 1/0.07Z. Then, the yarns were warped on a high speed warper (made by SUCKER), sized on a sizing machine (made by SUCKER), and woven on a high speed jet weaver (made by Tsuda Koma Industry Co., Ltd.) to prepare glass fiber fabric having the weave density of 44 warps/25m and 32 wefts/25mm. Then, the glass fiber fabric was hot de-oiled to remove the sizing agent, the fabric surface was treated with a silane coupling agent SZ 6032 (made by Dow Corning Toray Silicone Corp.) in the concentration of 0.30% by weight, and the fabric was impregnated with the FR-4 resin.

Table 1 about the stability of cake shape and the quality of glass fiber fabric shows that that glass fiber fabric had a very stable cake shape and exhibited excellent resin impregnation.

[0019] 〈 Example 2 〉

Etherified amylose-rich corn starch	3.5% by weight
Cross-linked normal corn starch	1.5% by weight
Hydrogenated cotton seed oil	1.0% by weight
Paraffin wax	1.0% by weight
Polyoxyethylene polyoxypropylene ether	0.2% by weight
Reaction product of tetraethylene pentamine with stearic acid	0.4% by weight
Formalin (an aqueous 4% by weight solution)	0.1% by weight
Colloidal silica (Cataloid S-30H made by Shokubai Kasei Kogyo Co., Ltd., having particle sizes of 10~20nm and SiO ₂ content of 30% by weight), as solids	0.5% by weight

Except that this sizing agent was applied to G75 glass fiber to the solid content of 0.90% by weight, the same procedure in Example 1 was repeated. Table 1 about the stability of cake shape and the quality of glass fiber fabric shows that that glass fiber fabric had a very stable cake shape and exhibited excellent resin impregnation.

[0020] 〈 Example 3 〉 Except that colloidal silica in Example 1 was replaced with 0.4% by weight of light precipitated calcium carbonate having the average particle size of 40nm, the same procedure in Example 1 was repeated. Test results are shown in Table 1.

[0021] 〈 Comparative Example 1 〉 Except that 0.5% by weight of colloidal silica in Example 1 was replaced with the addition of water, the same procedure in Example 1 was repeated. Test results are shown in Table 1.

[0022-missing]

[0023]

[Evaluation Procedures]

1. Shape Stability of Cake

The cake appearance was visually observed for classification into those with apparent deformation and those without deformation.

2. Fluff Inspection

The number of surface fluffing in the product after twisting, and the number of surface fluffing in glass fiber fabric woven on a weaver were counted for general judgement for 7 rank rating: the rank 1 had the least fluffing and the rank 7 had the maximum fluffing while the ranks 2 to less than 3 were sufficiently acceptable for the general application.

[0024] 3. Resin Impregnation

A predetermined amount (10mL) of a resin was dropped on de-oiled and surface-treated glass fiber fabric (10×10cm), and a time lapse until air bubbles were removed from the glass fiber fabric was determined for 7 rank rating: the smaller number shows that the better result was obtained.

Resin Composition Used

Epicoat 1001 (epoxy resin made by Shell Chemical) 100 parts by weight

Dicyandiamide 2 parts by weight

Benzyl dimethyl amine 0.2 part by weight

Methyloxytol 100 parts by weight

[0025]

[Advantage] According to the present invention, the external shape of wound up cakes is less deformed so that the breakage of glass fiber obtained can be reduced and the fluffing of yarns and glass fiber fabric can be reduced. Since solid particles are homogeneously deposited all over the glass fiber bundle constituting the glass fiber yarn, voids due to the solid particles can be secured among glass fibers even in the sections of glass fiber fabric where warps and wefts are the most densely crossing each other

to achieve the homogeneous resin impregnation and the reduction in the time period for resin impregnation.

[0026]

[Table 1]

	shape stability	fluffing (rating)	resin impregnation (rating)
Example 1	no deformation	1	1
Example 2	no deformation	2	1
Example 3	no deformation	2	2
Comparative Example 1	deformed	4	5

[End]